



Consommation  
et Corporations Canada

Consumer and  
Corporate Affairs Canada

Bureau des brevets

Patent Office

Ottawa, Canada  
K1A 0C9

(11) (C) **1,298,697**

(21) 549,819

(22) 1987/10/21

(45) 1992/04/14

(52) 31-9

<sup>5</sup>  
(51) INTL.CL. E21B-43/26

(19) (CA) **CANADIAN PATENT** (12)

(54) Viscoelastic Surfactant Gravel Carrier Fluids

(72) Nehmer, Warren L. , U.S.A.

(73) Dowell Schlumberger Incorporated , Canada

(30) (US) U.S.A. 079,727 1987/07/30

(57) 28 Claims

NO DRAWING

**Canada**

1298697

## VISCOELASTIC SURFACTANT GRAVEL CARRIER FLUIDS

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention:

This invention relates to aqueous viscoelastic surfactant based particle carrier fluids, corresponding particle slurries and methods of using the same in wellbore applications. More specifically, but not by way of limitation, the invention relates to the use of an organic salt (e.g., salicylate salt) or cosurfactants (e.g., aliphatic alcohols) to selectively control the loss of particle suspension properties of, and resulting complete particle settling from, a particle slurry as a function of temperature.

#### 2. Description of the Prior Art:

Essentially solids-free aqueous fluids containing electrolytes have some advantages over clay-based fluids for preparing wellbore service fluids because: (a) they do not normally contain undesirable solids which can cause formation damage, (b) they contain hydration inhibiting materials such as potassium chloride, ammonium chloride, calcium chloride or the like, which are important to prevent damage to clay containing formations, and (c) they can be prepared over a wide range of densities.

The viscosity of high electrolyte-containing aqueous fluids is, however, difficult to control because of the high electrolyte concentration. Thickened fluids are desirable for carrying solids, e.g., in cleaning out wells, drilling and the like. Likewise, thickened fluids resist water loss, which may be damaging to petroleum producing subterranean formations.

Hydroxy alkyl celluloses have been employed to thicken electrolyte-containing aqueous fluids to improve the solid carrying capacity thereof. Likewise, starch has been employed to aid in water loss control of these



fluids, but with limited success. However, these materials are difficult to disperse and dissolve in concentrated electrolytes at ambient temperature; the viscosity of the resulting solutions tends to decrease with an increase in temperature; and the hydroxy alkyl celluloses are subject to shear degradation under normal operating conditions.

Certain quaternary ammonium salts have been shown to impart viscoelastic properties to aqueous solutions, S. Gravsholt "Viscoelasticity in Highly Dilute Aqueous Solutions of Pure Cationic Detergents", Journal of Colloid and Interface Science, Vol.57, No.3, December 1976, pp.575-577. Gravsholt showed that cetyl trimethyl ammonium bromide would not impart viscoelastic properties to water but that cetyl trimethyl ammonium salicylate and certain other aromatic anion-containing quaternary amines would. In U.S. Patent 3,292,698, a mixture of cyclohexyl ammonium chloride and undecane-3-sodium sulfate was taught to induce viscoelastic properties to a formation flooding liquid containing less than about 3.5 percent by weight of sodium chloride. Higher levels of sodium chloride were said to destroy the viscoelastic properties of the fluid. In British Patent No. 1,443,244, a specific ethoxylated or propoxylated tertiary amine is employed to thicken an aqueous solution of a strong mineral acid. U.S. Patent 3,917,536 teaches that certain primary amines may be employed in subterranean formation acidizing solutions to retard the reaction of the acid on the formation. The amine may be more readily dispersed into the acid solution with the use of a dispersing agent such as a quaternary amine.

In particular, Canadian Patent 1,185,779 discloses a high electrolyte-containing aqueous wellbore service fluid which has improved viscosity characteristics over a wide range of wellbore conditions, including improved ease of

1298697

-3-

preparation at the well site and better shear stability  
and consistent viscosity over a wide temperature range.  
These improved aqueous wellbore service fluids are  
acknowledged as being useful in well known wellbore  
5 services such as perforation, clean-up, long term shut-in,  
drilling, placement of gravel packs and the like. These  
services are well known in the art and are taught, for  
example, in U.S. Patent Nos. 3,993,570; 3,176,950;  
3,126,950; 2,898,294, and in C.M. Hudgens et al, "High  
10 Density Packer Fluids Pay Off in South Louisiana"; World  
Oil, 1961, pp.113-119. The present invention is viewed as  
being an improvement over the compositions disclosed and  
taught in Canadian Patent 1,185,779 .

15 Also, as employed herein, "ppg" means pounds of  
particulate per gallon of slurry, and when "percent" or  
"%" is employed, it means percent by weight unless  
otherwise specified.

20  
  
25  
  
30  
  
35  
  
A

1298697

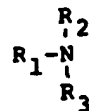
-4-

SUMMARY OF THE INVENTION

The present invention provides a method of adjusting a viscoelastic surfactant based particle carrier fluid and corresponding particle slurry such that the onset of the loss of particle suspension properties at specified temperatures is controlled. According to the present invention the yield point or low shear rate viscosity of viscoelastic surfactant fluids is controlled by the addition of salts and/or cosurfactants. Thus according to the present invention a given surfactant system can be used to prepare the viscous carrier fluid and then organic anions or cosurfactants can be added at varying concentrations to control the temperature stability of the gelled fluid. Because of the improved degree of control of the temperature at which settling of the suspended particulate material from the carrier fluid takes place, adequate particle transport and a resulting good particle placement can be more easily achieved. Consequently the present invention provides for greater flexibility and predictability in designing fluids and treatments for particle transport and placement.

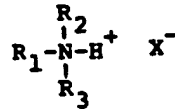
Thus the present invention provides an aqueous viscoelastic surfactant based particle pack slurry comprising:

- (a) water;
- (b) an effective amount of an inorganic water soluble salt to stabilize a subterranean formation by inhibiting hydration;
- (c) an effective amount of at least one thickener in the fluid, the thickener being at least one member selected from the group consisting of:
  - (i) an amine corresponding to the formula



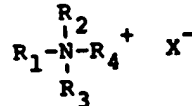
wherein  $R_1$  is at least about a  $C_{16}$  aliphatic group which may be branched or straight chained and which may be saturated or unsaturated,  $R_2$  and  $R_3$  are each independently, hydrogen or a  $C_1$  to about  $C_6$  aliphatic group which can be branched or straight chained, saturated or unsaturated and which may be substituted with a group which renders the  $R_2$  and/or  $R_3$  group more hydrophilic;

(ii) salts of the amine corresponding to the formula



wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same as defined hereinbefore and  $X^-$  is an inorganic anion, and;

(iii) a quaternary ammonium salt of the amine corresponding to the formula



wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $X^-$  are the same as hereinbefore defined and  $R_4$  independently constitutes a group which has previously been set forth for  $R_2$  and  $R_3$ , none of  $R_1$ ,  $R_2$ ,  $R_3$  or  $R_4$  are hydrogen, and the  $R_2$ ,  $R_3$  and  $R_4$  groups of the amine salt and quaternary ammonium salt may be formed into a heterocyclic 5 or 6 member ring structure which includes the nitrogen atom of the amine;

(d) an effective amount of an additive selected from the group consisting of an organic salt, a  $C_4$  to  $C_{12}$  aliphatic alcohol and mixtures thereof to control the time required for particle settling as a function of temperature; and

(e) an effective amount of particulate material.

1298697

-6-

It is an object of the present invention to provide a particle carrier fluid and particle slurry that exhibit an improved and predictable onset of complete particle settling as a function of temperature. It is a further  
5 object to provide a method of controlling the loss of the particle suspension properties of such particle slurry so as to predictably control particle settling. Fulfillment of these objects and the presence and fulfillment of other objects will be apparent upon complete reading of the  
10 enclosed specification and claims.

15

20

25

30

35

1298697

-7-

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention comprises an aqueous viscoelastic surfactant based particle fluid carrier and corresponding particle slurry. The particle pack fluid carrier involves water, an inorganic salt stabilizer, a surfactant/thickener and an organic salt or alcohol. A sufficient quantity of at least one water soluble salt to effect formation stability is employed. Typically water soluble potassium, ammonium and calcium salts, such as potassium chloride, ammonium chloride or calcium chloride, are employed. Formation stability and in particular clay stability is achieved at a concentration level of a few percent by weight and as such the density of the fluid is not significantly altered by the presence of the inorganic salt.

A sufficient quantity of at least one surfactant/thickener soluble in said aqueous salt solution is employed to effect, in combination with the organic salt and/or alcohol, sufficient viscosity to suspend the particles during the placement of the particulate material, wherein the thickener is at least one member selected from the group consisting of: (a) an amine corresponding to the formula



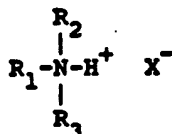
wherein  $R_1$  is at least about a  $C_{16}$  aliphatic group which may be branched or straight chained and which may be saturated or unsaturated;  $R_2$  and  $R_3$  are each independently, hydrogen or a  $C_1$  to about  $C_6$  aliphatic group which can be branched or straight chained, saturated or unsaturated and which may be substituted with a group which renders the  $R_2$  and/or  $R_3$  group more hydrophilic; (b) salts of the amine corresponding to the formula

35

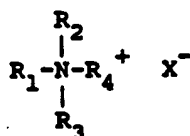


1298697

-8-



5 wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same as defined hereinbefore and  $X^-$  is an inorganic anion, and; (c) a quaternary ammonium salt of the amine corresponding to the formula



10 wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $X^-$  are the same as hereinbefore defined and  $R_4$  independently constitutes a group which has previously been set forth for  $R_2$  and  $R_3$ , none of  $R_1$ ,  $R_2$ ,  $R_3$  or  $R_4$  is hydrogen, and  
15 the  $R_2$ ,  $R_3$  and  $R_4$  groups of the amine salt and quaternary ammonium salt may be formed into a heterocyclic 5 or 6 member ring structure which includes the nitrogen atom of the amine.

A sufficient quantity of a water soluble organic  
20 salt and/or alcohol is employed to effect, in combination with the thickener, the desired viscoelastic properties as well as to effect control of the loss of particle suspension properties as a function of temperature. Preferably the organic salt is a water soluble  
25 carboxylate salt such as sodium or potassium salicylate or the like. Preferably the alcohol is a cosurfactant typically a  $C_4$  to  $C_{12}$  aliphatic alcohol.

A sufficient quantity of gravel or sand and the like, as generally known in the art, is then added to the  
30 viscoelastic carrier fluid to achieve the desired density for gravel pack placement.

The resulting gravel pack fluid slurry may have a weight of particulate material per gallon of slurry ranging from as low as about 1.0 ppg, up to about 15.0  
35 ppg. It is at these higher densities, that the practice

1298697

-9-

of the present invention is particularly useful. However, advantages are also achieved in the lower gravel content slurries.

5 Naturally occurring brines and seawater can be employed if desired. Preferably, the aqueous wellbore service fluid contains a few percent of a water soluble salt of potassium, ammonia or calcium. In addition, the aqueous fluid may contain other soluble salts of, for example, zinc, lithium, chromium, iron, copper, and the like. Preferably inorganic chlorides and/or bromides are employed but other salts such as sulfates, nitrates, etc. can be employed. The only restriction is that the salts must be compatible with the particular thickening agent employed to thicken the aqueous fluid. By compatible it is meant, for example, that the salt does not detrimentally interfere with the thickening function of thickening agent and/or undesirable quantities of precipitates are formed. As examples of useful water soluble salts reference <sup>may</sup> be had to Table 1 Column 3 of U.S. Patent No. 2,898,294.

20 One preferred aqueous particle carrier fluid contains up to a few percent of an inorganic salt such as KCl,  $\text{NH}_4\text{Cl}$ , or  $\text{CaCl}_2$  and a selected amount of an organic salt such as sodium salicylate. A preferred thickening agent for the above defined particle carrier fluid is a quaternary ammonium salt, N-methyl-N,N-bis(2-hydroxyethyl) rapessed ammonium chloried. Sufficient sand, typically 20/40 mesh, is then added to achieve the desired slurry density for placement in a wellbore.

25 30 The thickening agent employed in the invention comprises at least one of the thickening agents defined herinbefore under Summary of the Invention. It is found that with certain solutions, a mixture of two or more thickeners may be preferred.

1298697

-10-

In the cases where the thickening agent is an amine acid salt or a quaternary ammonium salt, an inorganic acid salt or anion is to be used. Preferably,  $X^-$  is an inorganic anion such as a sulfate, nitrate, perchlorate or halide. A halide, (Cl, Br or I) is preferred, Cl and Br being most preferred. In contrast to the compositions disclosed in the previously referenced Canadian Patent No. 1,185,779, the organic salt employed in the present invention contributes selectively the amount of organic anion present. This in turn leads to control of the viscoelastic properties and in particular, control of the loss of particle suspension properties of the carrier fluid.

The organic salt is preferably a water soluble compound involving typically a sodium or potassium salt of an organic anion. The anion may be an aromatic organic anion such as a salicylate, naphthalene sulfonate, p and m chlorobenzoates, 3,5 and 3,4 and 2,4-dichlorobenzoates, t-butyl and ethyl phenate, 2,6 and 2,5-dichlorophenates, 2,4,5-trichlorophenate, 2,3,5,6-tetrachlorophenate, p-methyl phenate, m-chlorophenate, 3,5,6-trichloropicolinate, 4-amino-3,5,6-trichloropicolinate, 2,4-dichlorophenoxyacetate, toluene sulfonate,  $\alpha$ ,  $\beta$ -naphthols or p,p'-bisphenol A. The thickening agent should be chosen such that the anion is compatible with the electrolyte present in the aqueous solution such that undesirable precipitates are not formed. Also the specific anion chosen will depend to some degree on the specific amine structure.

The thickening agent is employed in an amount which in combination with the other ingredients is sufficient to increase the viscosity of the aqueous fluid enough to maintain the particles in suspension during placement of the particulate material. The exact quantity and specific thickener or mixture of thickeners to be employed will

vary depending on the concentration of and specific soluble salt(s) employed to make up the solution, the viscosity desired, the temperature of use, the pH of the solution, and other similar factors. The concentration of the thickener can range from about 0.05 to about 5 percent, preferably from about 0.2 to about 3 percent of the aqueous wellbore service fluid. Simple laboratory procedures can be employed to determine the optimum conditions for any particular set of parameters. For example, when a non-protonated amine is employed as the thickener, the pH of the aqueous fluid can affect to some degree the effectiveness of particular amines. More acidic solutions are required for some amines to be dissolved therein. It is thought that this is because the amine must become protonated before it will become effectively dissolved in the fluid.

Examples of other thickeners which can be employed include oleyl methyl bis(hydroxyethyl) ammonium chloride; octadecyl methyl bis(hydroxyethyl) ammonium bromide; octadecyl tris(hydroxyethyl) ammonium bromide; and octadecyl dimethyl hydroxyethyl ammonium bromide; cetyl dimethyl hydroxyethyl ammonium bromide; cetyl methyl bis(hydroxyethyl) ammonium salicylate, cetyl methyl bis(hydroxyethyl) ammonium 3,4-dichlorobenzoate; cetyl tris(hydroxyethyl) ammonium iodide; bis(hydroxyethyl) soya amine; N-methyl, N-hydroxyethyl tallow amine; bis(hydroxyethyl) octadecyl amine; cosyl dimethyl hydroxyethyl ammonium bromide; cosyl methyl bis(hydroxyethyl) ammonium chloride; cosyl tris(hydroxyethyl) ammonium bromide; docosyl dimethyl hydroxyethyl ammonium bromide; docosyl methyl bis(hydroxyethyl) ammonium chloride; docosyl tris(hydroxyethyl) ammonium bromide; hexadecyl ethyl bis(hydroxyethyl) ammonium chloride, hexadecyl isopropyl bis(hydroxyethyl) ammonium iodide; N,N-dihydroxypropyl

1298697

-12-

hexadecyl amine, N-methyl, N-hydroxyethyl hexadecyl amine;  
N,N-dihydroxyethyl dihydroxypropyl oleyl amine;  
N,N-dihydroxypropyl soya amine; N,N-dihydroxypropyl tall w  
amine; N-butyl hexadecyl amine; N-hydroxyethyl octadecyl  
5 amine; N-hydroxyethyl cosyl amine; cetylamine, N-octadecyl  
pyridinium chloride; N-soya-N-ethyl morpholinium  
ethosulfate; methyl-1-oleyl amido ethyl-2-oleyl  
imidazolinium-methyl sulfate; methyl-1-tallow amido  
ethyl-2-tallow imidazolinium-methyl sulfate.

10 To prepare the aqueous particle carrier fluid of the  
present invention, the thickener is added to an aqueous  
solution to which has been dissolved a quantity of at  
least one water soluble inorganic salt to provide  
formation stability and at least one water soluble organic  
15 salt to provide selective control of the loss of particle  
suspension properties. Standard mixing procedures known  
in the art can be employed since heating of the solution  
and special agitation conditions are normally not  
necessary. Of course, if used under conditions of extreme  
20 cold such as found in Alaska, normal heating procedures  
should be employed. It has been found in some instances  
preferable to dissolve the thickener into a lower  
molecular weight alcohol prior to mixing it with the  
aqueous solution. The lower molecular weight alcohol  
25 (e.g., isopropanol) functions as an aid to solubilize the  
thickener. Other such agents can also be employed. A  
defoaming agent such as a polyglycol may be employed to  
prevent undesirable foam during the preparation of the  
service fluid.

30 In addition to the water soluble salts and thickening  
agents described hereinbefore, the aqueous wellbore  
service fluid may contain other conventional constituents  
which perform specific desired functions, e.g., corrosi n  
inhibitors, fluid loss additives, and the like. The  
35 gravel (e.g., sand) or other inert packing material can

1298697

-13-

then be suspended in the carrier fluid producing the desired gravel slurry.

5 The fluids defined herein can be employed in standard gravel pack treatment services employing techniques and equipment well known in the art. The following example illustrates the aqueous viscoelastic surfactant based particle carrier fluid and corresponding slurry.

EXAMPLE I

10 To 800 ml of an aqueous 2 weight percent KCl solution was added 32 ml of a 75% active solution of N-methyl-N,N-bis(2-hydroxyethyl) rapeseed ammonium chloride in isopropanol with stirring until all the surfactant dissolved. To four separate 200 ml aliquots of this non-viscous fluid was added 0.4, 0.6, 0.7 and 0.8  
15 grams of sodium salicylate. To 50 ml of each of the above solutions was added 90 grams of 20/40 mesh sand. The respective sand/fluid mixtures were stirred thoroughly in a 100 ml beaker to produce the equivalent of a 15 pound per gallon slurry. The beakers were then placed in a  
20 water bath and heated to a temperature of 100°F for testing the gravel suspension properties. The heated slurries were each then transferred to separate 50 ml graduated cylinders and the four graduated cylinders were placed in the water bath at 100°F. The time required for  
25 complete gravel settling to occur (i.e., the time required to achieve settling of approximately 34 ml of sand in the graduated cylinder with approximately 16 ml of clear fluid above the sand) was recorded. The process was then repeated using a 150°F water bath. The resulting data are  
30 presented in the following Table.

35

1298697

-14-

TABLE I

Run	Grams Sodium Salicylate	Molarity Sodium Salicylate	Time for Complete Settling (Minutes)	
			100°F	150°F
5				
1	0.4	0.0125	10	2
2	0.6	0.01875	24	6
3	0.7	0.02188	55	15
4	0.8	0.02500	72	17

10        The above data confirm that the rate of settling of the gravel from the gravel pack slurries according to the present invention is a function of the concentration of the organic salt and thus can be controlled by selecting the concentration of organic salt to be employed. It is

15        contemplated for purposes of this invention that the particular preferred range of organic salt to be used to achieve the desired degree and rate of gravel settling will vary slightly depending on the particular surfactant system and organic salt being used as well as the presence

20        of cosurfactants or other additives.

## EXAMPLE II

25        In a manner analogous to Example I, an aqueous 5 weight percent KCl solution was prepared using N-methyl-N,N-bis(2-hydroxyethyl) rapeseed ammonium chloride at the above specified concentration as the surfactant. To

30        separate aliquots of this fluid was added a series of four differing concentrations of pentanol and hexanol, respectively. Using 20/40 mesh sand, particle slurries were prepared to a density of 15 pounds per gallon of

35        slurry. The gravel suspension properties of each was then measured, again as described above, and the resulting data are presented in Tables II and III below.

1298697

-15-

TABLE II

	Run	% (Vol.) Pentanol	Time for Complete Settling (Minutes)	
			100°F	150°F
5	1	0.25	52	2
	2	0.50	67	1
	3	0.75	20	0.5
	4	1.00	15	0.5
10				

TABLE III

	Run	% (Vol.) Hexanol	Time for Complete Settling (Minutes)	
			100°F	150°F
15	1	0.125	31	5
	2	0.250	38	2
	3	0.375	17	0.5
	4	0.500	2	0.5
20				

25

Having thus described the invention with a certain degree of particularity, it is to be understood that the invention is not limited to the embodiments set forth herein for purposes of exemplification, but is to be limited only by the scope of the attached claims, including a full range of equivalents to which each element thereof is entitled.

30

35



I claim:

1. An aqueous viscoelastic surfactant based particle slurry comprising:

(a) water;

(b) an effective amount of an inorganic water soluble salt to stabilize a subterranean formation by inhibiting hydration;

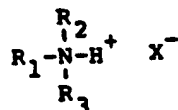
(c) an effective amount of at least one thickener in said fluid, said thickener being at least one member selected from the group consisting of:

(i) an amine corresponding to the formula



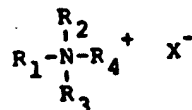
wherein  $R_1$  is at least about a  $C_{16}$  aliphatic group which may be branched or straight chained and which may be saturated or unsaturated,  $R_2$  and  $R_3$  are each independently, hydrogen or a  $C_1$  to about  $C_6$  aliphatic group which can be branched or straight chained, saturated or unsaturated and which may be substituted with a group which renders the  $R_2$  and/or  $R_3$  group more hydrophilic;

(ii) salts of said amine corresponding to the formula



wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same as defined hereinbefore and  $X^-$  is an inorganic anion, and;

(iii) a quaternary ammonium salt of said amine corresponding to the formula



wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $X^-$  are the same as

hereinbefore defined and  $R_4$  independently constitutes a group which has previously been set forth for  $R_2$  and  $R_3$ , none of  $R_1$ ,  $R_2$ ,  $R_3$  or  $R_4$  are hydrogen, and the  $R_2$ ,  $R_3$  and  $R_4$  groups of the amine salt and quaternary ammonium salt may be formed into a heterocyclic 5 or 6 member ring structure which includes the nitrogen atom of the amine;

(d) an effective amount of an additive selected from the group consisting of an organic salt, a  $C_4$  to  $C_{12}$  aliphatic alcohol and mixtures thereof to control the time required for particle settling as a function of temperature; and

(e) an amount of particulate gravel material effective in achieving a desired density for gravel pack placement.

2. An aqueous viscoelastic surfactant based particle slurry of claim 1 wherein the thickening agent is employed in an amount ranging from about 0.05 to about 5 percent of weight of the fluid.

3. An aqueous viscoelastic surfactant base particle slurry of claim 1 wherein the inorganic water soluble salt to stabilize a subterranean formation by inhibiting hydration is a potassium salt.

**1298697**

17a

71456-73

4. An aqueous viscoelastic surfactant based particle slurry of claim 1 wherein said additive is a salicylate salt.
5. An aqueous viscoelastic surfactant based particle slurry of claim 2 wherein said additive is a salicylate salt present in the range of from about 0.0125 molarity to about 0.025 molarity.
6. An aqueous viscoelastic surfactant based particle slurry of claim 5 wherein the inorganic salt is a potassium salt.
7. An aqueous viscoelastic surfactant based particle slurry of claim 6 wherein the thickener is N-methyl-N,N-bis(2-hydroxyethyl) rapeseed ammonium chloride.

1298697

-18-

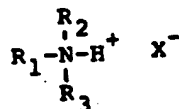
- 1 8. An aqueous viscoelastic surfactant based fluid  
2 comprising:  
3 (a) water;  
4 (b) an effective amount of an inorganic water  
5 soluble salt to stabilize a subterranean formation by  
6 inhibiting hydration;  
7 (c) an effective amount of at least one thickener in  
8 said fluid, said thickener being at least one member  
9 selected from the group consisting of:

10 (i) an amine corresponding to the formula



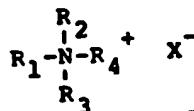
11  
12  
13 wherein  $R_1$  is at least about a  $C_{16}$  aliphatic  
14 group which may be branched or straight chained and  
15 which may be saturated or unsaturated,  $R_2$  and  $R_3$   
16 are each independently, hydrogen or a  $C_1$  to about  
17  $C_6$  aliphatic group which can be branched or  
18 straight chained, saturated or unsaturated and which  
19 may be substituted with a group which renders the  
20  $R_2$  and/or  $R_3$  group more hydrophilic;

21 (ii) salts of said amine corresponding to the  
22 formula



23  
24 wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same as defined  
25 hereinbefore and  $X^{-1}$  is an inorganic anion, and;

26 (iii) a quaternary ammonium salt of said amine  
27 corresponding to the formula



28  
29 wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $X^-$  are the same as  
30 hereinbefore defined and  $R_4$  independently  
31  
32  
33  
34  
35

36 constitutes a group which has previously been set  
37 forth for  $R_2$  and  $R_3$ , none of  $R_1$ ,  $R_2$ ,  $R_3$  or  
38  $R_4$  are hydrogen, and the  $R_2$ ,  $R_3$  and  $R_4$  groups  
39 of the amine salt and quaternary ammonium salt may be  
40 formed into a heterocyclic 5 or 6 member ring  
41 structure which includes the nitrogen atom of the  
42 amine; and

43 (d) an effective amount of an additive selected from  
44 the group consisting of an organic salt, a  $C_4$  to  
45  $C_{12}$  aliphatic alcohol and mixtures thereof to  
46 control the time required for gravel settling as a  
47 function of temperature.

1 9. An aqueous viscoelastic surfactant based slurry of  
2 claim 8 wherein the thickening agent is employed in an  
3 amount ranging from about 0.05 to about 5 percent by  
4 weight of the fluid.

1 10. An aqueous viscoelastic surfactant based slurry of  
2 claim 8 wherein the inorganic water soluble salt to  
3 stabilize a subterranean formation by inhibiting hydration  
4 is a potassium salt.

1 11. An aqueous viscoelastic surfactant based slurry of  
2 claim 8 wherein said additive is a salicylate salt.

1 12. An aqueous viscoelastic surfactant based slurry of  
2 claim 9 wherein said additive is a salicylate salt present  
3 in the range of from about 0.0125 molarity to about 0.025  
4 molarity.

1 13. An aqueous viscoelastic surfactant based slurry of  
2 claim 12 wherein the inorganic salt is a potassium salt.

1 14. An aqueous viscoelastic surfactant based slurry of  
2 claim 13 wherein the thickener is N-methyl-N,N-bis  
3 (2-hydroxyethyl) rapeseed ammonium chloride.

1 15. A method of treating a subterranean formation  
2 comprising the steps of:

- 3 (a) providing a particle fluid slurry of Claim 1;  
4 (b) injecting said fluid slurry downhole such as t

1298697

- 20 -

71456-73

position the gravel at the desired subterranean location;

(c) maintaining said fluid slurry at the desired location until complete settling takes place.

16. A method of claim 15 wherein the thickening agent is employed in an amount ranging from about 0.05 to about 5 percent by weight of the fluid.

17. A method of claim 15 wherein the inorganic water soluble salt to stabilize a subterranean formation by inhibiting hydration is a potassium salt.

18. A method of claim 15 wherein said additive is a salicylate salt.

19. A method of claim 16 wherein said additive is a salicylate salt present in the range of from about 0.0125 molarity to about 0.025 molarity.

20. A method of claim 19 wherein the inorganic salt is a potassium salt.

21. A method of claim 20 wherein the thickener is N-methyl-N,N-bis(2-hydroxyethyl) rapeseed ammonium chloride.

22. A method of controlling the time necessary to effect complete particulate material settling from a particle slurry as a

X

1298697

- 20a -

71456-73

function of temperature comprising the steps of:

(a) providing a particle slurry comprising

(i) water

(ii) an effective amount of an inorganic water soluble salt to stabilize a subterranean formation by inhibiting hydration;

(iii) an effective amount of at least one thickener in said fluid, said thickener being at least one member selected from the group consisting of:

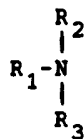
(x) an amine corresponding to the formula

X

1298697

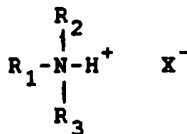
21

71456-73



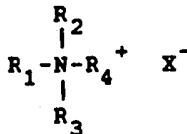
wherein  $R_1$  is at least about a  $C_{16}$  aliphatic group which may be branched or straight chained and which may be saturated or unsaturated,  $R_2$  and  $R_3$  are each independently, hydrogen or a  $C_1$  to about  $C_6$  aliphatic group which can be branched or straight chained, saturated or unsaturated and which may be substituted with a group which renders the  $R_2$  and/or  $R_3$  group more hydrophilic;

(y) salts of said amine corresponding to the formula



wherein  $R_1$ ,  $R_2$  and  $R_3$  are the same as defined hereinbefore and  $X^-$  is an inorganic anion, and;

(z) a quaternary ammonium salt of said amine corresponding to the formula





1298697

21a

71456-73

wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $X^-$  are the same as hereinbefore defined and  $R_4$  independently constitutes a group which has previously been set forth for  $R_2$  and  $R_3$ , none of  $R_1$ ,  $R_2$ ,  $R_3$  or  $R_4$  are hydrogen, and the  $R_2$ ,  $R_3$  and  $R_4$  groups of the amine salt and quaternary ammonium salt may be formed into a heterocyclic 5 or 6 member ring structure which includes the nitrogen atom of the amine;

(iv) an amount of particulate gravel material effective in achieving a desired density for gravel pack placement; and

(b) adding to said particle slurry an effective

1298697

-22-

- 51 amount of an additive selected from the group  
52 consisting of an organic salt, a C<sub>4</sub> to C<sub>12</sub>  
53 aliphatic alcohol and mixtures thereof to achieve the  
54 desired time of complete particle settling as a  
55 function of temperature.
- 1 23. A method of claim 22 wherein the thickening agent is  
2 employed in an amount ranging from about 0.05 to about 5  
3 percent by weight of the fluid.
- 1 24. A method of claim 22 wherein the inorganic water  
2 soluble salt to stabilize a subterranean formation by  
3 inhibiting hydration is a potassium salt.
- 1 25. A method of claim 22 wherein said additive is a  
2 salicylate salt.
- 1 26. A method of claim 23 wherein said additive is a  
2 salicylate salt present in the range of from about 0.0125  
3 molarity to about 0.025 molarity.
- 1 27. A method of claim 26 wherein the inorganic salt is a  
2 potassium salt.
- 1 28. A method of claim 27 wherein the thickener is  
2 N-methyl-N,N-bis(2-hydroxyethyl) rapeseed ammonium  
3 chloride.

Smart & Biggar  
Ottawa, Canada  
Patent Agents

